

MODELING BREAKTHROUGH OF NITROGEN HETEROCYCLIC COMPOUNDS IN LABORATORY COLUMNS CONTAINING CREOSOTE- CONTAMINATED AQUIFER MATERIAL

by

[Ean Warren](#) and E. Michael Godsy

U.S. Geological Survey
345 Middlefield Road, MS480
Menlo Park, CA 94025

Published in: Morganwalp, D.W. and Aronson, D.A., eds., U.S. Geological Survey Toxic Substances Hydrology Program–Proceedings of the Technical Meeting, Colorado Springs, Colorado, September 20-24, 1993: U.S. Geological Survey Water-Resources Investigations Report 94-4015, vol. 2, p. 851-858.

Click [here](#) to go to U.S. Geological Survey's Water Resources Division, National Research Program.

MODELING BREAKTHROUGH OF NITROGEN HETEROCYCLIC COMPOUNDS IN LABORATORY COLUMNS CONTAINING CREOSOTE-CONTAMINATED AQUIFER MATERIAL

by [Ean Warren](#) and E. Michael Godsy

ABSTRACT

Laboratory-column breakthrough curves for the nitrogen-containing heterocyclic compounds found in the water soluble fraction of creosote were modeled and compared assuming local equilibrium and nonequilibrium conditions. The aquifer material consisted of a low organic-carbon-content (0.024 percent organic carbon), low ion-exchange-capacity (2 meq/100 g) clayey sand. Retardation factors and partition coefficients for quinoline, 2(1H)-quinolinone, carbazole, and acridine, derived from breakthrough curves, were contrasted with those obtained from batch experiments. Retardation factors for quinoline and 2(1H)-quinolinone were comparable to each other, although those for carbazole and acridine were quite different despite similar chemical structures and octanol-water partition coefficients. Transport of quinoline, 2(1H)-quinolinone, and acridine is governed by organic and ionic interactions; however, transport of carbazole is controlled by organic interactions alone. In addition, although the local equilibrium assumption can be used to describe quinoline and 2(1H)-quinolinone breakthrough curves, carbazole and acridine breakthrough curves require nonequilibrium kinetics.

INTRODUCTION

Modeling is necessary to predict the fate and transport of organic contaminants in aquifers. Model parameters must be estimated or determined either from field studies or laboratory experiments. Commonly, model input data are generated from properties of water that are not comparable to the properties of ground water at the site of contamination. Ground-water characteristics, such as pH, must be compared to ionization constants (pK_a) to determine the effects of the sediment's ion exchange capacity. Simulated transport will not be accurate if the parameter at a pH differs from that of the ground water. In addition, laboratory studies commonly yield values for parameters using methods that do not reflect field conditions. For example, batch or column studies are used to determine partition coefficients, even though batch studies, often performed without considering the rate at which equilibrium is approached, do not consider nonequilibrium partitioning between aqueous and solid phases and column studies do not necessarily use representative packing or ground-water velocities.

In this paper, we compare the values of partition coefficients and retardation factors for quinoline, 2(1H)-quinolinone, carbazole, and acridine by two different laboratory methods on low organic-carbon-content, low ion-exchange capacity aquifer material. The partition coefficients and retardation factors vary with the measurement method, most notably for acridine. In addition, we compare the results obtained for different equilibrium assumptions used in modeling column effluent. Column effluents were modeled successfully using the local equilibrium assumption for quinoline and 2(1H)-quinolinone and the nonequilibrium assumption for carbazole and acridine. Column studies are preferred over equilibrium batch studies because column studies yield more data under conditions similar to those in the field. However, to determine sorption rate constants

independently, batch experiments measuring the rate at which equilibrium is attained must be conducted in conjunction with column experiments (Ball and Roberts, 1991b).

Site description

The study-site aquifer consists of quartz sand and gravel with interspersed silt and clay lenses (Franks, 1988). During 1902-81, wood-treatment wastes were discarded into impoundments that were in direct contact with the ground water. Creosote and pentachlorophenol wastes migrated vertically into the subsurface. The ground water, at a pH of approximately 5.9 and moving at a speed of about 1 m/d, continually dissolved the more soluble compounds in creosote creating an extended water soluble fraction (WSF) contamination plume. A major fraction of the WSF consists of the nitrogen heterocycles (for example, quinoline, carbazole, and acridine, as well as 2(1H)-quinolinone, a microbial degradation product) (Godsy and others, 1992).

Models

The transport of the WSF in laboratory columns can be described by the convection-dispersion equation using the local equilibrium assumption (LEA) as proposed by Hashimoto and others (1964)--

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = R \frac{\partial C}{\partial t}, \quad (1)$$

where

D is the dispersion coefficient [m^2/d],

C is aqueous concentration [g/m^3],

v is linear velocity [m/d],

x is distance [m],

t is time [d], and

R relates the movement of a contaminant to a conservative tracer [-].

Equation 1 assumes a linear Freundlich isotherm (Freundlich, 1926)--

$$\bar{C} = K_d C, \quad (2)$$

where

\bar{C} is mass concentration of contaminant adsorbed onto the adsorbent [g/g] and

K_d relates aqueous concentration to sorbed concentration [m^3/g].

Retardation factors, R , and partition coefficients, K_d , are related by

$$R = 1 + \frac{\rho_b K_d}{\theta}, \quad (3)$$

where

ρ_b is the bulk density of the aquifer material [g/m^3] and

θ is the porosity [-].

Transport commonly must be modeled using the nonequilibrium assumption (NEA) as proposed by van Genuchten and Wierenga (1976), which accounts for a readily mobile fraction and a stagnant or immobile fraction of water in the aquifer matrix (subscripts m and im , respectively)--

$$(\theta_m + f \rho_b K_d) \frac{\partial C_m}{\partial t} + [\theta_{im} + (1 - f) \rho_b K_d] \frac{\partial C_{im}}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - v_m \theta_m \frac{\partial C_m}{\partial x} \quad (4)$$

$$[\theta_{im} + (1 - f) \rho_b K_d] \frac{\partial C_{im}}{\partial t} = \alpha_1 (C_m - C_{im}). \quad (5)$$

where

f is the fraction of sorption sites in the mobile region [-] and

α_1 defines the transfer rate of the solute between mobile and immobile water [d^{-1}].

The model is based on the assumption that convection and dispersion govern transport in the mobile water and diffusion controls the transfer of contaminant between mobile and immobile water. The model includes two fitted dimensionless parameters: ω , the ratio of hydrodynamic residence time to characteristic time of sorption (Brusseau and Reid, 1991); and β , the relative contribution of the sites accessible to mobile water to the overall retardation. The original coefficients, α_1 and f , relate to ω and β as follows:

$$f = \beta + \frac{\theta\beta - \theta_m}{\rho_b K_d} \quad (6)$$

$$\alpha_1 = \frac{\omega q}{L}, \quad (7)$$

where

q is the flux rate [$m^3/m^2 \cdot d$] and

L is characteristic length [m].

MATERIALS AND METHODS

Aquifer materials were collected from a site upgradient from the contaminant plume. The samples were washed with 10 mM calcium chloride ($CaCl_2$), pH 5.9 before being dried in an oven at $104^\circ C$ to prevent dilution by residual water. This $CaCl_2$ concentration and pH closely parallel the ionic strength and pH of the natural ground water at the study site. Aquifer-material characteristics are given in table 1.

Organic-carbon content of the aquifer material was measured by the Walkley-Black Method (Walkley and Black, 1934) as described in Methods of Soil Analysis (Black and others, 1965, p. 1372). Cation-exchange capacity of the aquifer material was determined by the method of Black and others (1965, p. 899) using ion chromatography.

Aqueous samples were analyzed for organic compounds by reverse phase high-performance liquid chromatography (HPLC) using gradient elution of 5 to 100 percent acetonitrile in 26 mM ammonium acetate, pH 7.6 on a C-18 column with a diode-array detector.

The batch studies involved five different concentrations (table 2), in duplicate, of quinoline, 2(1H)-quinolinone, and acridine in 15 mM $CaCl_2$ (pH 5.9), sterilized through a filter with a 0.45- μm pore size, and added to autoclaved 10 mL serum bottles with and without aquifer material. The serum bottles were sealed with Teflon-lined butyl rubber septa and aluminum crimp seals. The samples were first shaken rapidly for 2 days at room temperature ($23 \pm 2^\circ C$) and then allowed to equilibrate in the dark at room temperature with intermittent shaking before sampling. Samples were checked for equilibrium conditions by periodically sacrificing bottles of the same concentration. The concentration of the compounds in the bottles with aquifer material was compared to the concentration in the bottles without aquifer material to determine the mass of compound adsorbed onto the aquifer material. Samples were checked for sterility at the end of the experiment. No bacterial contamination was found.

Columns were prepared using dried aquifer material. The aquifer material was first passed through a 1.0 mm sieve, removing less than 0.3 percent by weight. The sediment was dampened slightly to aggragate the material and packed into a glass column, 1 to 3 mm at a time, as

described by Goerlitz (1984). The column characteristics are given in table 1. A constant-flow HPLC syringe pump was connected to the influent end of the column and a variable wavelength UV detector and a refractometer were connected to the effluent end. All the fittings and tubing were either glass, stainless steel, or Teflon. All CaCl_2 solutions were degassed and filtered before use. Ten mM CaCl_2 at pH 5.9 was pumped through the column until the column reached equilibrium. The compounds were dissolved into 15 mM CaCl_2 at pH 5.9 and run through the column at approximately $120 \times 10^{-6} \text{ m}^3/\text{d}$ until the CaCl_2 concentration in the effluent equaled that in the influent (table 2). This flow rate is approximately equal to a linear velocity of 1 m/d in the aquifer.

Parameters— R for the LEA and R , β , and ω for NEA—were fit to the breakthrough curves (BTC's) using nonlinear regression analysis. BTC's were analyzed by use of the computer program HASHPE (Oravitz, 1984) to determine LEA parameters and the computer program CFITIM (van Genuchten, 1981) to determine NEA parameters. The dispersion parameter for all model simulations was determined from CaCl_2 breakthrough.

RESULTS

Batch Studies

Linear Freundlich partition coefficients for batch studies of quinoline, 2(1H)-quinolinone, and acridine were determined by linear regression (with the y-intercept forced to zero) on the aqueous and sorbed concentrations (table 3). The r^2 values for acridine and 2(1H)-quinolinone were 0.95. The r^2 value for quinoline was 0.85. This value is low because quinoline exhibited nonlinear sorption, confirming that reported by Zachara and others (1986). Despite this, the local equilibrium model, which is based on the assumption of linearity, closely reproduced quinoline in the column effluent, possibly because of a low selectivity coefficient.

Column Studies

Retardation factors for quinoline and 2(1H)-quinolinone were similar (table 3). 2(1H)-Quinolinone, with a pK_a of 5.29 (table 3), is approximately 20 percent ionized and quinoline, with a pK_a of 4.9, is approximately 9.1 percent ionized. Zachara and others (1986) have shown that sorption of quinoline is dominated by ion exchange up to 2 pH units above its pK_a . 2(1H)-Quinolinone, like quinoline, should be retained by ion exchange and organic sorption.

The retardation of acridine is significantly higher than that of carbazole despite the fact that both have two benzene rings fused to a nitrogen heterocyclic ring (fig. 1) and have similar octanol-water partition coefficients (table 3). However, the pK_a of acridine is 5.6 and that of carbazole is -5.7 (table 3). Thus, at pH 5.9, the ionized fraction of acridine is 0.33, but carbazole is completely un-ionized. The degree of affinity of acridine to charged functional groups on the aquifer material (the selectivity coefficient) and the extent of ionization as well as the cation-exchange capacity contributes to the exchange capacity. With an acridine concentration of 18 g/m^3 (0.10 meq/L), the column capacity due to ion exchange is 160. The column capacity is based on the assumption of total sorption of the ionized fraction of acridine to the aquifer material and complete displacement of calcium ions.

LEA and NEA Models

Breakthrough curves for quinoline, 2(1H)-quinolinone, carbazole, and acridine were modeled using both LEA and NEA. The BTC's for 2(1H)-quinolinone and the conservative tracer, CaCl_2 ,

for both LEA and NEA fitted models are shown in figure 2. LEA and NEA models are indistinguishable.

The BTC for acridine along with LEA and NEA fitted models are shown in figure 3. The LEA model does not follow the BTC at any time. Carbazole gave similar results (data not shown). The results indicate that, under flow conditions similar to that at the study site, transport of acridine and carbazole is controlled by nonequilibrium conditions and transport of quinoline and 2(1H)-quinolinone is controlled by equilibrium conditions.

Fitted parameters and original coefficients for quinoline, 2(1H)-quinolinone, carbazole, and acridine using the NEA model are given in table 4. The values of β for carbazole and acridine agree with each other. The value of ω for carbazole, however, is about twice that for acridine, indicating that the characteristic time of sorption contributes more to acridine transport than to carbazole transport.

DISCUSSION AND CONCLUSION

Transport of nitrogen heterocycles is governed by the retardation and the rate at which equilibrium is approached, both of which must be determined to model transport and sorption processes properly. The values of both parameters used in models depend on ground-water pH, water velocities, and contaminant concentrations, among other factors. To reduce error in the laboratory studies, these variables must be similar to that of the ground water at the contaminated site. The effects of ion exchange can have a profound effect on transport of weakly acidic or basic compounds. Transport under nonequilibrium conditions will also affect initial breakthrough and tailing. Without accurate laboratory-generated data, models may produce erroneous results.

In this study, parameter values determined from batch and column studies for quinoline and 2(1H)-quinolinone, compounds with low octanol-water partition coefficients, were similar. However, the two methods gave quite different results for acridine. This is to be expected because equilibrium batch studies give values for LEA parameters and column studies under conditions similar to those in the field give values for NEA parameters. Batch or column studies are often used to generate model parameters. Both types of studies have advantages and disadvantages. Batch experiments have been criticized as (1) using a large liquid to sediment ratio and improperly represented sediment characteristics (Barrow and Shaw, 1975; Sparks, 1985; Ball and Roberts, 1991a; Kookana and others, 1992), and (2) not modeling actual flow-field conditions (Freeze and Cherry, 1979; Ball and Roberts, 1991b). Column experiments commonly are subject to unrealistic flows and packing (Johnson and Farmer, 1993) and cannot determine the specific reason for nonequilibrium transport.

Although retardation factors for quinoline and 2(1H)-quinolinone, both of which are partially ionized, were comparable, those for carbazole and acridine were quite different. This difference indicates that ion exchange plays a large role in the transport of contaminants in the aquifer material. This study shows that transport of quinoline, 2(1H)-quinolinone, and acridine is governed by ionic and organic interactions, but that carbazole is controlled by organic interactions alone.

The LEA model sufficiently describes the column effluent for quinoline and 2(1H)-quinolinone. However, the NEA model must be used for carbazole and acridine. Brusseau and Rao (1989) suggest that, for values of ω less than 10, the NEA should be used instead of the LEA. The values of ω for carbazole and acridine are well below the value suggested by Brusseau and Rao,

justifying the use of the NEA model. Godsy (1993) observed that NEA provides a better fit to data when the $\log K_{ow}$ is greater than 2.5. The specific reason for nonequilibrium–diffusion between mobile and immobile water and (or) the kinetics of sorption to organic or ionic sites–cannot be determined from BTC analysis and must be resolved by rate batch studies. Column models show the importance of nonequilibrium in describing transport of contaminants. Equilibrium batch studies, on the other hand, do not indicate whether a contaminant, under field flow conditions, is actually at equilibrium. This distinction is important when modeling transport in the ground water.

REFERENCES

- American Petroleum Institute, 1979, Quinoline: API Monograph Series, Publication 711, Washington, D.C., American Petroleum Institute, 43 p.
- American Petroleum Institute, 1981, Carbazole, 9-Methylcarbazole, and Acridine: API Monograph Series, Publication 716, Washington, D.C., American Petroleum Institute, 51 p.
- Ball, W.P. and Roberts, P.V., 1991a, Long-term sorption of halogenated organic chemicals by aquifer material. 1. Equilibrium: *Environmental Science & Technology*, v. 25, no. 7, p. 1223-1237.
- Ball, W.P. and Roberts, P.V., 1991b, Long-term sorption of halogenated organic chemicals by aquifer material. 2. Intraparticle diffusion: *Environmental Science & Technology*, v. 25, no. 7, p. 1237-1249.
- Barrow, N.J. and Shaw, T.C., 1975, The slow reactions between soil and anions: 5. Effects of period of prior contact on the desorption of phosphate from soils: *Soil Science*, v. 119, no. 4, p. 311-320.
- Black, C.A., Evans, D.D., White, J.L., Ensminger, L.E., and Clark, F.E., eds., 1965, *Methods of Soil Analysis, Part 2, Agronomy*: Madison, Wisconsin, American Society of Agronomy, 1572 p.
- Brusseau, M.L. and Rao, P.S.C., 1989, The influence of sorbate-organic matter interactions on sorption nonequilibrium: *Chemosphere*, v. 18, no. 9-10, p. 1691-1706.
- Brusseau, M.L. and Reid, M.E., 1991, Nonequilibrium sorption of organic chemicals by low organic-carbon aquifer materials: *Chemosphere*, v. 22, no. 3-4, p. 341-350.
- Franks, B.J., 1988, *Hydrogeology and flow of water in a sand and gravel aquifer contaminated by wood-preserving compounds*, Pensacola, Florida: U.S. Geological Survey Water-Resources Investigations Report 87-4260, 72 p.
- Freeze, R.A. and Cherry, J.A., 1979, *Groundwater*: Englewood Cliffs, N.J., Prentice-Hall, 604 p.
- Freundlich, Herbert, 1926, *Colloid and Capillary Chemistry*: London, Methuen.
- Godsy, E.M., 1993, *Methanogenic biodegradation of creosote-derived contaminants in natural and simulated ground water ecosystems*: Stanford, Calif., Stanford University, Ph.D. dissertation, 173 p.
- Godsy, E.M., Goerlitz, D.F., and Grbić-Galić, Dunja, 1992, Methanogenic biodegradation of creosote contaminants in natural and simulated ground-water ecosystems: *Ground Water*, v. 30, no. 2, p. 232-242.
- Goerlitz, D.F., 1984, A column technique for determining sorption of organic solutes on the lithological structure of aquifers: *Bulletin of Environmental Contamination and Toxicology*, v. 32, p. 37-44.

- Hansch, Corwin and Leo, A.J., 1979, Substituent Constants for Correlation Analysis in Chemistry and Biology: New York, John Wiley and Sons.
- Hashimoto, I., Deshpande, K.B., and Thomas, H.C., 1964, Peclet numbers and retardation factors for ion exchange columns: *Industrial Engineering Chemical Fundamentals*, v. 3, p. 213-218.
- Johnson, J.A. and Farmer, W.J., 1993, Batch versus column method for determining distribution of organics between soil and water phases: *Soil Science*, v. 155, no. 2, p. 92-99.
- Kookana, R.S., Gerritse, R.G., and Aylmore, L.A.G., 1992, A method for studying nonequilibrium sorption during transport of pesticides in soil: *Soil Science*, v. 154, no. 5, p. 344-349.
- Oravitz, J.L., 1984, Transport of trace organics with one-dimensional saturated flow: Mathematical modeling and parameter sensitivity analysis: Michigan Technological University, M.S.C.E. Thesis, Department of Civil Engineering.
- Sparks, D.L., 1985, Kinetics of ionic reactions in clay minerals and soils: *Advances in Agronomy*, v. 38, p. 231-266.
- Stecher, P.G., Windholz, Martha, Leahy, D.S., Bolton, D.M., and Eaton, L.G., eds., 1968, *The Merck Index* (8th ed.): Rahway, N.J., Merck & Co., Inc., 1713 p.
- van Genuchten, M.T., 1981, Non-Equilibrium Transport Parameters from Miscible Displacement Experiments: U.S. Department of Agriculture, U.S. Salinity Laboratory Research Report 119, 88 p.
- van Genuchten, M.T. and Wierenga, P.J., 1976, Mass transfer studies in sorbing porous media. I. Analytical solution: *Soil Science Society of America Proceedings*, v. 40, p. 473-480.
- Walkley, A. and Black, I.A., 1934, An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method: *Soil Science*, v. 37, p. 29-38.
- Zachara, J.M., Ainsworth, C.C., Felice, L.J., and Resch, C.T., 1986, Quinoline sorption to subsurface materials: role of pH and retention of the organic cation: *Environmental Science and Technology*, v. 20, p. 620-627.

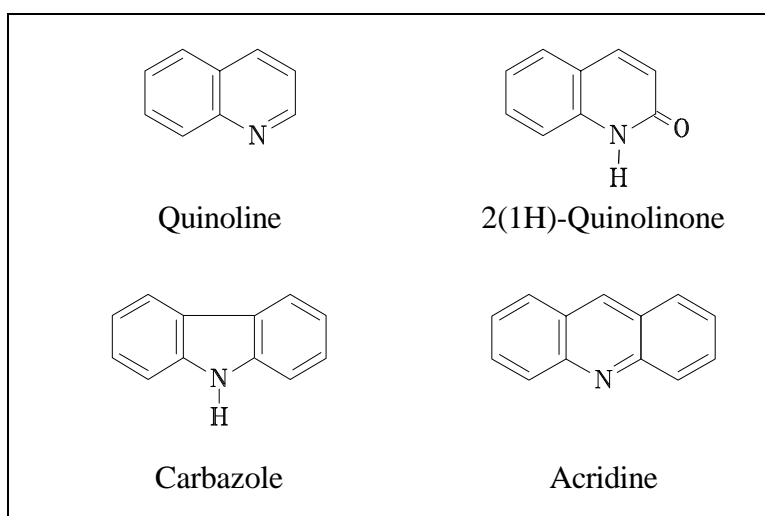


Figure 1.--Chemical structures of quinoline, 2(1H)-quinolinone, carbazole, and acridine.

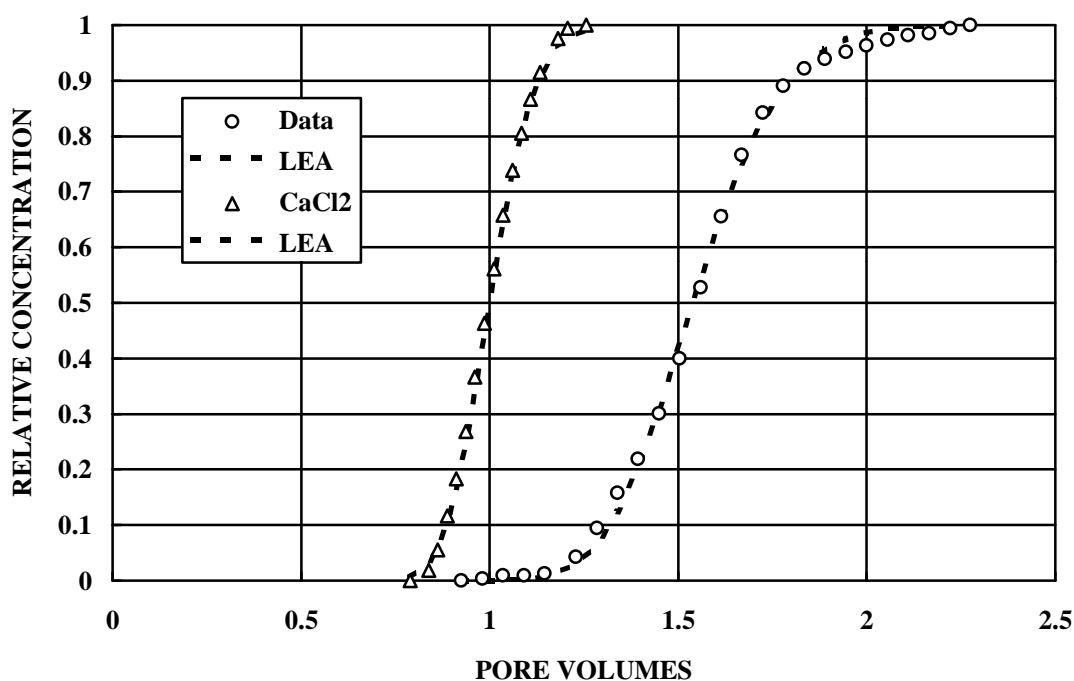


Figure 2.--Calcium chloride (CaCl₂) and 2(1H)-quinolinone breakthrough curves from column data and fitted local equilibrium assumption model (LEA). Because local equilibrium assumption and nonequilibrium assumption models for 2(1H)-quinolinone can be superimposed on each other, the nonequilibrium assumption model is not shown.

Relative concentrations [-] were calculated using $\frac{C - C_0}{C_i - C_0}$, where C is the effluent concentration, C_0 is the original concentration at the start of the experiment, and C_i is the influent concentration. Pore volumes [-] were determined by dividing time by the time it takes for one-half of the relative concentration of CaCl₂ to move through the column.

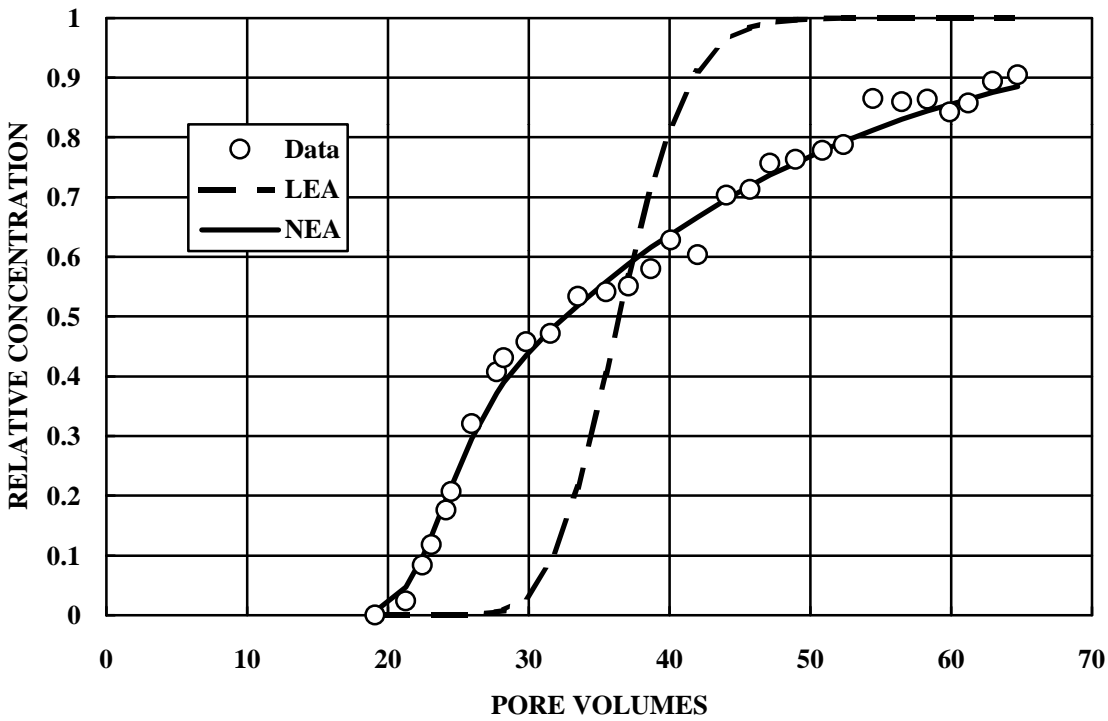


Figure 3.--Acridine breakthrough curves from column data and local equilibrium (LEA) and nonequilibrium (NEA) assumption fitted models. Relative concentrations [-] were calculated using $\frac{C - C_0}{C_i - C_0}$ where C is the effluent concentration, C_0 is the original concentration at the start of the experiment, and C_i is the influent concentration. Pore volumes [-] were determined by dividing time by the time it takes for one-half of the relative concentration of CaCl_2 to move through the column.

Table 1.--Aquifer material and column characteristics

[m, meter; meq/100 g, milliequivalents per 100 grams; g/m³, gram per cubic meter; m³/d, cubic meter per day]

Median Particle Diameter [m]	0.000375
Percent Organic Carbon [-]	.024
Cation Exchange Capacity [meq/100 g]	1.6
<u>Column</u>	
Length [m]	0.354
Diameter [m]	.025
Porosity [-]	.449
Bulk Density [g/m ³ x 10 ⁻⁶]	1.361
Flow Rate [m ³ /d x 10 ⁶]	140

Table 2.--Concentrations of quinoline, 2(1H)-quinolinone, carbazole, and acridine for batch and column studies

[Concentrations in gram per cubic meter]

	Batch					Column
Quinoline	140	72	30	9.3	1.7	2.5
2(1H)-Quinolinone	53	26	9.7	3.2	0.60	2.5
Carbazole						8.9
Acridine	35	19	9.4	2.6	0.47	18

Table 3.-- pK_a , $\log K_{ow}$, partition coefficients, and retardation factors for quinoline, 2(1H)-quinolinone, carbazole, and acridine

[Partition coefficients in cubic meter per gram x 10⁶]

	pK_a ¹	$\log K_{ow}$ ²	Partition coefficient ³	<u>Retardation factor</u>	
				Batch ⁴	Column ⁵
Quinoline	4.90	2.03	0.133	1.40	1.32
2(1H)-Quinolinone	5.29	1.26	.231	1.70	1.54
Carbazole	-5.70	3.29			4.32
Acridine	5.60	3.40	4.56	14.8	39.6

¹ (Stecher and others, 1968, p. 210; American Petroleum Institute, 1979; American Petroleum Institute, 1981).

² (Hansch and Leo, 1979).

³ Determined using linear regression on the aqueous and sorbed batch concentrations.

⁴ Calculated using equation 3.

⁵ Determined using local equilibrium assumption for quinoline and 2(1H)-quinolinone and nonequilibrium assumption for carbazole and acridine.

Table 4.--Nonequilibrium assumption parameter values for quinoline, 2(1H)-quinolinone, carbazole, and acridine

	β	f^1	ω	α_1^2
Quinoline	0.0	0.0	160	110
2(1H)-Quinolinone	.0	.0	1300	900
Carbazole	.60	.60	2.6	1.8
Acridine	.61	.61	1.2	0.81

¹ Calculated assuming $\theta\beta-\theta_m$ equals zero (van Genuchten and Wierenga, 1976) in equation 6.

² Calculated using equation 7.